

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Improvements in or relating to Complex Ester Synthetic Lubricants

We, ESSO RESEARCH AND ENGINEERING COMPANY, formerly known as Standard Oil Development Company, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to synthetic lubricating compositions. Particularly the invention relates to new and useful synthetic lubricants that have outstanding utility at both high and low temperatures and that have, in addition, low carbonization characteristics and result in little or no sludge formation when used in automotive engines.

In recent efforts to obtain superior lubricating compositions which have unusual and specific properties, there have been developed entirely new synthetic materials. In general, these new synthetic lubricants are characterized by viscosity properties that are outstanding at both high and low temperatures, especially when compared to mineral oils. These outstanding low and high temperature properties are especially desirable for use in equipment designed to operate over a great temperature differential, such as jet engines for aircraft use, combustion engines for aircraft and the like. It has been found that mineral lubricating oils are generally undesirable for the lubrication of these engines because of their high and low temperature viscosity limitations.

It has also been found that synthetic lubricants may be desirable for the lubricating of standard automotive engines. In addition to the versatility of their viscosities, the use of some types of the synthetic lubricants investigated have been found to result in very low rates of combustion chamber deposit forma-

tion, particularly when used for long periods of time. These combustion chamber deposits usually occur in the form of carbonaceous deposits on the combustion chamber surfaces. Low rates of formation of combustion chamber deposits result in increased power factor from fuel, less increase in the octane requirement of the engine, less preignition tendency and a general overall improvement in engine operation.

It has been found that for use in reciprocating engines, particularly as a lubricant for automotive engines, a lubricating composition must meet several requirements. In order to form an effective lubricating film and to maintain that film at low and high temperatures, it must have certain viscosity characteristics. At low temperatures, it must have certain viscosity characteristics. At low temperatures, the lubricant must be sufficiently mobile to flow through the circulatory system of the equipment and allow movement of lubricated surfaces without undue power requirement. A lubricant having an ASTM pour point below about +35° F. has sufficient low temperature lability to make it satisfactory in these respects for general use. At high temperatures a lubricant must have sufficient "body" or "thickness" to furnish and maintain a satisfactory lubricating film. It has been found that a lubricant that is satisfactory in this respect will have a viscosity at 210° F. of between about 2 and 60 centistokes or 32.8 and 280 Saybolt Seconds Universal. To prevent undue lubricant loss, due to volatility and general molecular disintegration, and to insure against explosion hazards at high temperatures sometimes encountered, a lubricating composition should have a flash point in excess of about 300° F. The preferred complex esters of the present invention and mixtures thereof have a viscosity within the range of 2 to 60 centistokes at 210° F., an A.S.T.M. pour point below 35° F. and a flash point above 300° F.

[Price 3s. 0d.]

Price 3s. 6d.

Price 4s. 6d.

The especially preferred complex esters of the present invention and mixtures thereof have an A.S.T.M. pour point below  $-15^{\circ}\text{F.}$ , a flash point above  $375^{\circ}\text{F.}$ , and will have viscosities within the range of 2.6 to 15 centistokes, or 35 to 78 Saybolt Seconds Universal at  $210^{\circ}\text{F.}$

For the purposes of this specification complex esters are defined as liquid polyesters containing no free hydroxyl, thiol or carboxyl groups, and in which hypothetical replacement of the ether oxygen atoms of the ester groups and any ether oxygen atoms and any sulphide sulphur atoms that may be present by methylene groups would produce a polyketone with four or more carbonyl groups in the same carbon chain.

It has been discovered and this discovery forms the basis of the present invention that complex esters which are particularly suitable as lubricants are those which contain at least one saturated aliphatic hydroxy monocarboxylic acid residue or at least one saturated aliphatic mercapto monocarboxylic acid residue, at least one residue selected from saturated aliphatic monohydric alcohol, saturated aliphatic monocarboxylic acid or saturated aliphatic monomercaptan residues, and at least one saturated aliphatic dicarboxylic acid residue. The complex ester contains at least two hydroxy acid or mercapto acid residues or at least one glycol residue which is not joined to an hydroxy acid residue via an ether linkage. The term glycol residue joined to an hydroxy acid residue via an ether linkage as used herein is shown in the formula  $-\text{O}-\text{R}-\text{O}-\text{R}^1-\text{CO.O}-$ . The complex esters of the present invention do not contain this linkage. An hydroxy acid residue and glycol residue may be joined via an ester linkage as shown in the formula  $-\text{O}-\text{R}-\text{O}-\text{CO}-\text{R}^1-\text{O}-$ , where R is the glycol residue and  $\text{R}^1$  is the hydroxy acid residue.

Preferred materials for preparing the complex esters of this invention are as follows:—

1. Monohydric alcohols or mercaptans represented by the formula



wherein X is oxygen or sulfur and wherein R is an alkyl group containing from 1 to 20 carbon atoms.

2 Aliphatic dibasic acids of the formula



wherein y is a whole number preferably from 2 to 8.

3. Dibasic acids of the formula



wherein p is a whole number preferably from 1 to 8, and X is either oxygen or sulfur.

4. Glycols of the formula



wherein n is a whole number greater than 1, preferably 2 to 5 and wherein y is a whole number, preferably from 1 to 20.

5. Monobasic acids of the formula



wherein R is a saturated aliphatic group containing from 1 to 20 carbon atoms, preferably an alkyl radical.

6. Mercapto- or hydroxy-acids of the formula



wherein R is hydrogen or an alkyl group containing from 1 to 10 carbon atoms, X is oxygen or sulfur, and wherein z is a whole number, preferably 1 to 12.

Using these starting materials it is possible to build compositions having the desired lubricating characteristics. Some of the preferred types of contemplated complex esters are depicted by the formulae below:—

#### TYPE

- 1 alcohol-hydroxy acid-dibasic acid-hydroxy acid-alcohol
- 2 monobasic acid-hydroxy acid-glycol-dibasic acid alcohol 85
- 3 monobasic acid glycol-hydroxy acid-dibasic acid-alcohol
- 4 alcohol-dibasic acid-hydroxy acid-glycol-dibasic acid-alcohol 90
- 5 alcohol-dibasic acid-hydroxy acid-glycol hydroxy acid-dibasic acid-alcohol
- 6 alcohol-hydroxy acid-dibasic acid-glycol-hydroxy acid-dibasic acid-alcohol
- 7 alcohol-dibasic acid-hydroxy acid-glycol hydroxy acid-monobasic-acid 95
- 8 alcohol-hydroxy acid-dibasic acid-glycol-dibasic acid-hydroxy acid-alcohol
- 9 alcohol-hydroxy acid-dibasic acid-glycol-dibasic acid-alcohol 100

In the above types of complex esters "mercaptan" may be used instead of "alcohol" and "mercapto-acid" may be substituted for "hydroxy-acid".

The preferred complex esters of the above type contain a total of from 20 to 130 carbon atoms per molecule, with from 25 to 100 carbon atoms per molecule being especially satisfactory.

A partial list of the aliphatic alcohols operable in the preparation of the complex esters of this invention will include the following alcohols: methyl, ethyl, propyl, isopropyl, n-butyl, iso-butyl, sec.-butyl, tert.-butyl, n-amyl, iso-amyl, n-hexyl, isohexyl, 2-ethyl-1-butyl, 2-ethyl-1-hexyl, octyl, iso-octyl, 2-octyl, iso-nonyl, decyl, lauryl, tetradecyl, pentadecyl, octadecyl, the  $\text{C}_{20}$  to  $\text{C}_{25}$  Oxo alcohols, alcohols derived from the Synol process, those derived from the oxidation of petroleum fractions, those derived from the Guerbet reaction, those derived from the hydration of olefins, those derived via the "Oxyl" synthesis, and the mixtures of the above. The corresponding mercaptans may also be used. Especially preferred are those alcohols and mercaptans containing from 6 to 10 carbon atoms.

Particularly desirable alcohols for use in this invention are those highly branched chain

aliphatic alcohols prepared by the "Oxo" synthesis. The "Oxo" synthesis may be described as being the catalytic reaction of an olefin with carbon monoxide and hydrogen.

- 5 The reaction occurs at temperatures in the order of 40—200° C., at pressures in the range of 20—300 atmospheres, in the presence of a suitable catalyst, ordinarily a heavy metal carbonyl such as cobalt carbonyl. The resulting aldehyde is subsequently hydrogenated to a primary alcohol. This process is described in U.S. Patent No. 2,327,066 issued to Roelen in 1943.

- It has been found that particularly desirable alcohols for the formation of the complex esters of this invention can be prepared by the application of the Oxo synthesis to polymers and copolymers of C<sub>3</sub> and C<sub>4</sub> monoolefins. These monoolefins are readily available in petroleum refinery streams, and processes for their conversion to liquid copolymers have been worked out by the art. One such process, known as U.O.P. polymerization, consists of passing the olefin-containing stream in liquid phase in contact with an acid catalyst comprising phosphoric acid impregnated on kieselguhr. Other acidic catalysts, such as phosphoric acid or copper phosphate impregnated on silica gel, sulfuric acid, Friedel-Crafts catalysts, activated clays, silica-alumina, and copper pyrophosphate, may be used. Suitable conditions when employing phosphoric acid catalysts of the U.O.P. type are temperatures of 300° F. to 500° F., pressures from 250 to 5000 psi and feed stocks comprising refinery streams containing propylene and mixed butylenes. Suitable feed stocks, for example, may contain from 15 to 60 mol percent propylene, from 0.5 to 15 mol percent butylenes, and from 0.1 to 10 mol percent isobutylene, the remainder being saturated hydrocarbons. Other suitable feed stocks are the dimer and trimer of isobutylene.

- The preferred Oxo alcohols employed in this invention are those having from 8 to 20 carbon atoms derived from olefin copolymers having from 7 to 19 carbon atoms. In preparing these Oxo alcohols the desired olefin fraction is segregated from the crude olefin polymer product by fractionation.

- The following table, for example, shows the structure and percent composition of C<sub>8</sub> Oxo alcohols prepared from a C<sub>7</sub> olefin stream which had been fractionated from the products obtained by the phosphoric acid polymerization of refinery gas streams containing propylene and mixed *n*- and isobutylenes.

Structure of C<sub>8</sub> Oxo alcohols prepared from C<sub>3</sub>—C<sub>4</sub> copolymer heptenes

	Percent	60
$\begin{array}{c} \text{C} \quad \text{C} \\   \quad   \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$	- -	29
$\begin{array}{c} \text{C} \quad \text{C} \\   \quad   \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$	- -	25
$\begin{array}{c} \text{C} \quad \text{C} \\   \quad   \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$	- -	17
$\begin{array}{c} \text{C} \\   \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$	}	16
$\begin{array}{c} \text{C} \\   \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$		
$\begin{array}{c} \text{C} \\   \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$	- -	2.3
$\begin{array}{c} \text{C} \\   \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$	- -	1.4
$\begin{array}{c} \text{C} \\   \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH} \end{array}$	- -	4.3
γ-alkyl-alkanols	- - - - -	5.0
Others	- - - - -	
		100.0

It will be noted that Oxo alcohols derived from the olefins produced by C<sub>3</sub>—C<sub>4</sub> polymerization are mostly methyl substituted.

Dibasic acids operable in the concept of this invention include the following: malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, diglycolic, thiodiglycolic, and thiodipropionic. Especially preferred are those dibasic acids containing from 6 to 10 carbon atoms.

Operable glycols include: ethylene glycol, the various diols, such as propane-, butane-, pentane- and hexanediols, and polyalkylene glycols such as polyethylene glycols and polypropylene glycols. Especially preferred are the glycols and polyalkylene glycols of the formula:—



wherein  $n$  is an integer from 2 to 5 and where  $y$  is an integer of from 1 to 20.

- Operable monobasic acids include the following: acetic, propionic, butyric, 2-ethylbutyric, caproic, 2-ethyl hexanoic, caprylic, pelargonic, capric, lauric, myristic, stearic, methoxy propionic, ethoxyethoxy-acetic, mono-2-ethyl hexyl adipate, mono- $C_8$  Oxo sebacate, acids derived from alcohols by caustic fusion, acids derived from petroleum fractions by oxidation, and mixtures of the above. Those acids containing from 4 to 10 carbon atoms are preferred.

- Operable hydroxy- and mercapto- acids include the following: hydroxy-acetic (glycolic), gamma hydroxy-butyric, alpha hydroxy-caproic, alpha hydroxy-caprylic, alpha hydroxy-propionic (lactic), beta-hydroxy-propionic, 12-hydroxy-stearic, and the corresponding mercapto acids, such as thio-glycolic acid.

The preparation of the complex esters of this invention may be accomplished by either a one-step or a two-step technique.

- It will be noted from examination of the various types of the complex esters contemplated as described above, that these esters are "terminated", or "stopped" by use of a monofunctional material, either an alcohol, mercaptan or a monobasic acid. In the two-step technique, the central or "body" portion of the complex ester may be prepared in a first step by admixing the desired amount of the chosen reactants with a small amount of a catalyst and a water entrainer in reaction zone. The catalyst may be any of the commonly known esterification catalysts, such as sodium acid sulfate, toluene sulfonic acid, sulfosalicylic acid; sulfuric acid, or zinc chloride. The reaction temperature is maintained at about 150° to about 220° C. for from 2 to 6 hours, or until tests of the reaction mixture show that the esterification is substantially completed. In the second step, the "stopping" or "terminating" agent, either a monobasic acid or a monohydric alcohol or mercaptan is added in the correct amount. The reaction temperature is then maintained at about 200° to about 230° C. to complete the reaction.

- However it may also be desired to prepare a half ester of a bifunctional material and then connect two mols of such half ester with a second bifunctional material. For example, the first step of such a procedure might be to react together equi-molar quantities of an alcohol and a hydroxy acid and then react together two mols of the resulting ester with one mol of a dibasic acid in a second step. Other variations available will be apparent to those skilled in the art.

- Purification of the complex ester is accomplished by stripping off any unreacted ingredients, water entrainer, light ends and the like by a stripping step. Vacuum stripping may be desired in some instances. The material,

stripped as above, may then be washed to remove any residual acidity with an alkaline solution, such as a sodium carbonate solution. Final acidity may also be reduced to the desired level by filtration through alumina or charcoal or some similar adsorbent material.

In the one-step process, referred to above, the theoretical amount of all the desired reactants plus any excess are added to the reaction zone and the temperature maintained at about 190° to 230° C. to complete the reaction. The same general finishing procedures as outlined above may be used to prepare the final product, that is, a stripping step, using vacuum if desired, a washing step, and an alumina or charcoal treatment.

It may also be desired to add antioxidants to the esterification reaction or at other points in the process of preparing these complex ester synthetic lubricants. The antioxidant prevents deterioration, by oxygen of the reactants or product during the esterification. Such materials as phenothiazine have been found to aid in the preparation of more desirable lubricants.

The invention will be more clearly explained by reference to the following illustrative examples:—

#### EXAMPLE I.

PREPARATION OF TYPE 4 COMPLEX ESTER (2-ETHYL-HEXANOL-SEBACIC ACID-GLYCOLIC ACID-POLYETHYLENE GLYCOL — SEBACIC ACID-2-ETHYLHEXANOL)

In this preparation a one-step procedure was employed. The following ingredients were charged to a 3—1 esterification apparatus equipped with stirrer, thermometer, reflux condenser and water trap.

Sebacic acid	- - -	606 g.	105
Polyethylene glycol (m. wt. of 200)	- - -	273 g.	
Glycolic acid (70%)	- - -	164 g.	
2-ethylhexanol	- - -	390 g.	
10% excess 2-ethylhexanol	- - -	39 g.	110
Phenothiazine (0.5%)	- - -	6.5 g.	
Heptane	- - -	55 g.	
NaHSO <sub>4</sub> catalyst (0.5%)	- - -	6.5 g.	

These ingredients were heated to reflux temperature and after 3 hours the temperature had gradually increased to 210° C. and 187 cc. of water had collected. The crude ester was then heat treated at 235° C. for 3 hours during which time the pressure was lowered to 10 mm. to remove the volatile constituents. After washing with 10% Na<sub>2</sub>CO<sub>3</sub> aqueous solution and alcohol, followed by two water washes, the material was filtered and then stripped to 162° C. at 8 mm. to give 1140 g. of lubricant having the following properties:—

Viscosity Cs. @ °F.			
	210	-	14.05
	100	-	86.7
	0	-	4350
5	-40	-	94400
	V.I.	-	139
	Pour point, ° F.	-	-45
	Flash point, ° F.	-	530
	Fire point, ° F.	-	570
10	1 hr. SOD lead corrosion loss, mg.	-	61
	SAE-SOD load test, lbs.*	-	700
*SAE Lubricant Tester is run in at 50 lb. load for 2 minutes, then load is increased manually by 50 lbs. every 10 seconds until scuffing of bearing rings occurs.			
15			

## EXAMPLE II.

PREPARATION OF TYPE 1 COMPLEX ESTER (C <sub>10</sub> OXO ALCOHOL-GLYCOLIC ACID-SEBACIC ACID-GLYCOLIC ACID-C <sub>10</sub> OXO ALCOHOL.)			
20	The following ingredients were used:—		
	Sebacic acid	-	202 g.
	Glycolic acid (70%)	-	218 g.
25	C <sub>10</sub> Oxo alcohol (by oxonation and hydrogenation of tripropylene	-	316 g.
	10% excess C <sub>10</sub> Oxo alcohol	-	32 g.
	Heptane	-	57 g.
	NaHSO <sub>4</sub> catalyst (0.5%)	-	3.0 g.
30	The C <sub>10</sub> Oxo glycolate was made by heating everything except the sebacic acid to 177° C. over a 1 hour period. The water collected was 100 cc. The sebacic acid was then added and the esterification continued to get 36.5 cc. more water by carrying the esterification temperature to 190° C. The material was then decanted from the catalyst sludge, washed with two 600 cc. portions of 2.5% Na <sub>2</sub> CO <sub>3</sub> solution and two 200 cc. portions of water and then stripped to 212° C. kettle temperature at 0.25 mm. pressure. The product had the following properties:—		
	Kin. Vis./210° F. Cs.	-	7.32
	100° F.	-	46.25
45	0° F.	-	2520
	-40° F.	-	51100
	V.I.	-	125
	Pour point, ° F.	-	-45
	Flash point, ° F.	-	510
50	Fire point, ° F.	-	560

It is also within the concept of this invention to prepare synthetic lubricating compositions which comprise blends of the complex ester synthetic lubricants as described above with various of the additive materials used by the art to enhance special lubricating characteristics of the final blend. For instance, these complex esters may be blended with viscosity index improvers such as polybutene, and polyacrylate and polymethacrylate esters containing from 8 to 18 carbon atoms in the alcohol groups. These complex esters may also be blended with pour point depressants such as wax naphthalene condensation products,

acrylate and methacrylate ester polymers, fumarate-vinyl ester copolymers. Other additives, such as detergent inhibitors, anti-rust agents, extreme pressure additives, and oxidation inhibitors may also be blended with these synthetic esters.

The synthetic lubricants of this invention may also be used to compound various blends using as a blending agent other synthetic lubricants such as formals, polyalkylene ethers, dibasic acid esters, silicones, silicates, polyglycol ethers, and ether-esters. The complex esters of this invention may be blended with mineral lubricating oils of either naphthenic or paraffinic origin.

The complex esters of this invention may also be used as the base oils for the formation of lubricating grease compositions. Greases from these esters may be prepared by thickening them with any of the commonly used grease-forming soaps, such as the alkali or alkaline earth metal soaps of high molecular weight fatty acids. Soaps such as the oleates, stearates, or hydroxy stearates of sodium, potassium, lithium, calcium, barium, or strontium may be used. Soaps formed by heating animal, fish or vegetable oils with derivatives of the above metals may also be used.

The complex esters of the invention are preferably those having viscosities at 210° F. within the range of from 2.6 to 15 centistokes ASTM pour points below about 35° F., and flash points above about 300° F. Especially preferred and contemplated in the preferred embodiment hereof are those complex esters having the formula:—

$$\text{RXC}(\text{CH}_2)_z\text{CHXCR}_2\text{CXCH}(\text{CH}_2)_z\text{CXR}_4$$

wherein R and R<sub>4</sub> are alkyl radicals containing from 1 to 20 carbon atoms, preferably 6 to 12 carbon atoms, R<sub>2</sub> is a divalent saturated hydrocarbon radical containing from 1 to 20 carbon atoms and preferably from 6 to 12 carbon atoms, R<sub>1</sub> and R<sub>3</sub> are hydrogen atoms or alkyl radicals containing from 1 to 10 carbon atoms; wherein X is oxygen or sulfur, wherein z is an integer from 1 to 12, preferably 4 to 6, and

$$\text{R}^1\text{XCR}_2^1\text{CXCH}(\text{CH}_2)_z^1\text{COR}_3^1\text{OCR}_4^1\text{CXR}_5^1$$

wherein R<sup>1</sup> and R<sub>5</sub><sup>1</sup> are alkyl groups containing from 1 to 20 carbon atoms, preferably from 6 to 12 carbon atoms, wherein R<sub>1</sub><sup>1</sup> is hydrogen or an alkyl radical containing from 1 to 10 carbon atoms, R<sub>2</sub><sup>1</sup> and R<sub>4</sub><sup>1</sup> are saturated divalent hydrocarbon radicals containing from 1 to 20 carbon atoms, preferably from 6 to 12 carbon atoms, R<sub>3</sub><sup>1</sup> is a saturated divalent hydrocarbon radical containing from 2 to 20 carbon atoms, preferably from 6 to 12 carbon atoms, or a polyethyleneoxy radical, wherein X is oxygen or sulfur and wherein z<sup>1</sup> is an integer from 1 to 12, preferably 4 to 6.

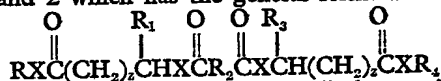
A preferred complex ester is one in which  $R^1$  and  $R_5^1$  are branched chain alkyl groups containing 8 carbon atoms,  $R_2^1$  and  $R_4^1$  are saturated divalent hydrocarbon radicals containing 6 carbon atoms,  $R_1^1$  is hydrogen and  $R_3^1$  is a polyethyleneoxy radical or a divalent hydrocarbon radical containing from 6 to 12 carbon atoms, X is oxygen and  $z^1$  is 1.

What we claim is:—

- 10 1. A complex ester containing at least one saturated aliphatic hydroxy monocarboxylic acid residue or at least one saturated aliphatic mercapto monocarboxylic acid residue, at least one residue selected from saturated aliphatic monohydric alcohol, saturated aliphatic monocarboxylic acid or saturated aliphatic monomercaptan residues, and at least one saturated aliphatic dicarboxylic acid residue, the said complex ester containing at least two
- 15 of the hydroxy acid or mercapto acid residues or at least one glycol residue, any glycol residue present not being joined to the hydroxy group of the hydroxy acid residue via an ether linkage, the said complex ester being a liquid
- 20 polyester containing no free hydroxyl, thiol or carboxyl groups and in which hypothetical replacement of the ether oxygen atoms of the ester groups and of any ether oxygen atoms and any sulphide sulphur atoms, that may be present by methylene groups would produce a polyketone with four or more carbonyl groups in the same carbon chain.

2. A complex ester as claimed in Claim 1 which contains from 20 to 130 carbon atoms.

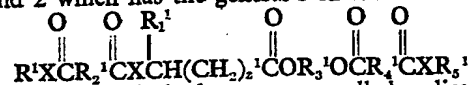
- 25 3. A complex ester as claimed in Claims 1 and 2 which has the general formula



- 30 wherein R and  $R_4$  are alkyl radicals containing from 1 to 20 carbon atoms and  $R_1$  and  $R_3$  are hydrogen atoms or alkyl radicals containing from 1 to 10 carbon atoms and  $R_2$  is a divalent saturated hydrocarbon radical containing from 1 to 20 carbon atoms,  $z$  is an integer from 1 to 12, and X is oxygen or sulphur.
- 45 4. A complex ester as claimed in claim 3 in which R, and  $R_4$  are alkyl radicals containing from 6 to 10 carbon atoms,  $R_2$  is a divalent saturated hydrocarbon radical containing from 6 to 12 carbon atoms,  $R_1$  and  $R_3$  are alkyl radicals containing from 1 to 10 carbon atoms X is oxygen and  $z$  is an integer from 4 to 6.

5. A complex ester as claimed in Claim 3 in which R and  $R_4$  are branched chain alkyl groups containing 10 carbon atoms,  $R_1$  and  $R_3$  are hydrogen atoms,  $R_2$  is a saturated divalent hydrocarbon radical containing 6 carbon atoms,  $z$  is 1 and X is oxygen.

6. A complex ester as claimed in Claims 1 and 2 which has the general formula



in which  $R_1^1$  is hydrogen or an alkyl radical containing from 1 to 10 carbon atoms,  $R^1$  and  $R_5^1$  are alkyl groups containing from 1 to 20 carbon atoms,  $R_2^1$  and  $R_4^1$  are saturated divalent hydrocarbon radicals containing from 1 to 20 carbon atoms,  $R_3^1$  is a saturated divalent hydrocarbon radical containing from 2 to 20 carbon atoms or a polyethyleneoxy radical, X is oxygen or sulphur and  $z^1$  is an integer from 1 to 12.

7. A complex ester as claimed in Claim 6 in which  $R_1^1$  is hydrogen,  $R^1$  and  $R_5^1$  are alkyl groups containing from 6 to 10 carbon atoms,  $R_2^1$ ,  $R_3^1$  and  $R_4^1$  are saturated divalent hydrocarbon radicals containing from 6 to 12 carbon atoms,  $z^1$  is an integer from 4 to 6 and X is oxygen.

8. A complex ester as claimed in Claim 6 in which  $R^1$  and  $R_5^1$  are branched chain alkyl groups containing 8 carbon atoms,  $R_2^1$  and  $R_4^1$  are saturated divalent hydrocarbon radicals containing 6 carbon atoms,  $R_1^1$  is hydrogen and  $R_3^1$  is a polyethyleneoxy radical. X is oxygen and  $z$  is 1.

9. A complex ester as claimed in any of Claims 1 to 8 which has an A.S.T.M. pour point below 35° F., a flash point above 300° F. and a viscosity at 210° F. within the range of 2 to 60 centistokes.

10. A lubricating composition comprising the complex esters claimed in any of Claims 1 to 9.

11. A lubricating composition as claimed in Claim 10 which contains phenothiazine.

12. A complex ester, a process of preparing complex esters and a lubricating composition comprising said complex esters substantially as hereinbefore described with particular reference to the examples.

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